IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of

Piotr KULA et al.	Group Art Unit: 1742
Application No.: 10/531,690	Examiner: W. ZHU
Filed: April 15, 2004	Docket No.: 122083

For: HYDROGEN GAS MIXTURE FOR THE UNDER-PRESSURE CARBURIZING OF STEEL

DECLARATION UNDER 37 C.F.R. §1.132

I, Piotr Kula, a citizen of Poland, hereby declare and state:

1.   I have a degree in mechanical engineering, materials science and heat treating of metals which was conferred upon me by Politechnika Lodzka (Poland) in 1975.

2.   I have been employed by Politechnika Lodzka since 1975 (since 1996 as professor), and I have had a total of 20 years experience in the field of steel carburizing.

3.   I am a named inventor in the above-captioned patent application. I am familiar with the patent application.

4.   I have a professional relationship with the Assignee, Seco/Warwick SP.ZO.O. and Politechnika Lodzka, of the above-identified patent application. In the course of that professional relationship, I received compensation directly from Seco/Warwick SP.ZO.O and Politechnika Lodzka for my work relating to research and development regarding steel carburization.

5.   I and/or those under my direct supervision and control have conducted the following experiment, which uses acetylene, ethylene and hydrogen at various compositions and proportions to carburize steel in a low pressure vacuum furnace chamber.

The experimental results demonstrate that the presently claimed acetylene/ethylene/hydrogen mixture for under-pressure carburizing steel achieves unexpected results in an intensive hydrocarbon decomposition along with an efficient carbon transfer at an acetylene to ethylene ratio of 0.55 when compared to Japanese Patent Publication No. 2000-001765 (hereinafter "JP 765") in which a gas mixture with a different ratio of acetylene to ethylene (only 0.428) is used to vacuum carburize steel.

The charge containing low carbon steel sheets and three 17CrNi samples of total surface area of 0.4 m^2 were treated in the vacuum carburizing furnace. The furnace, experimental equipment and the investigated charge are illustrated below in Figures 1(a) to 1(d).
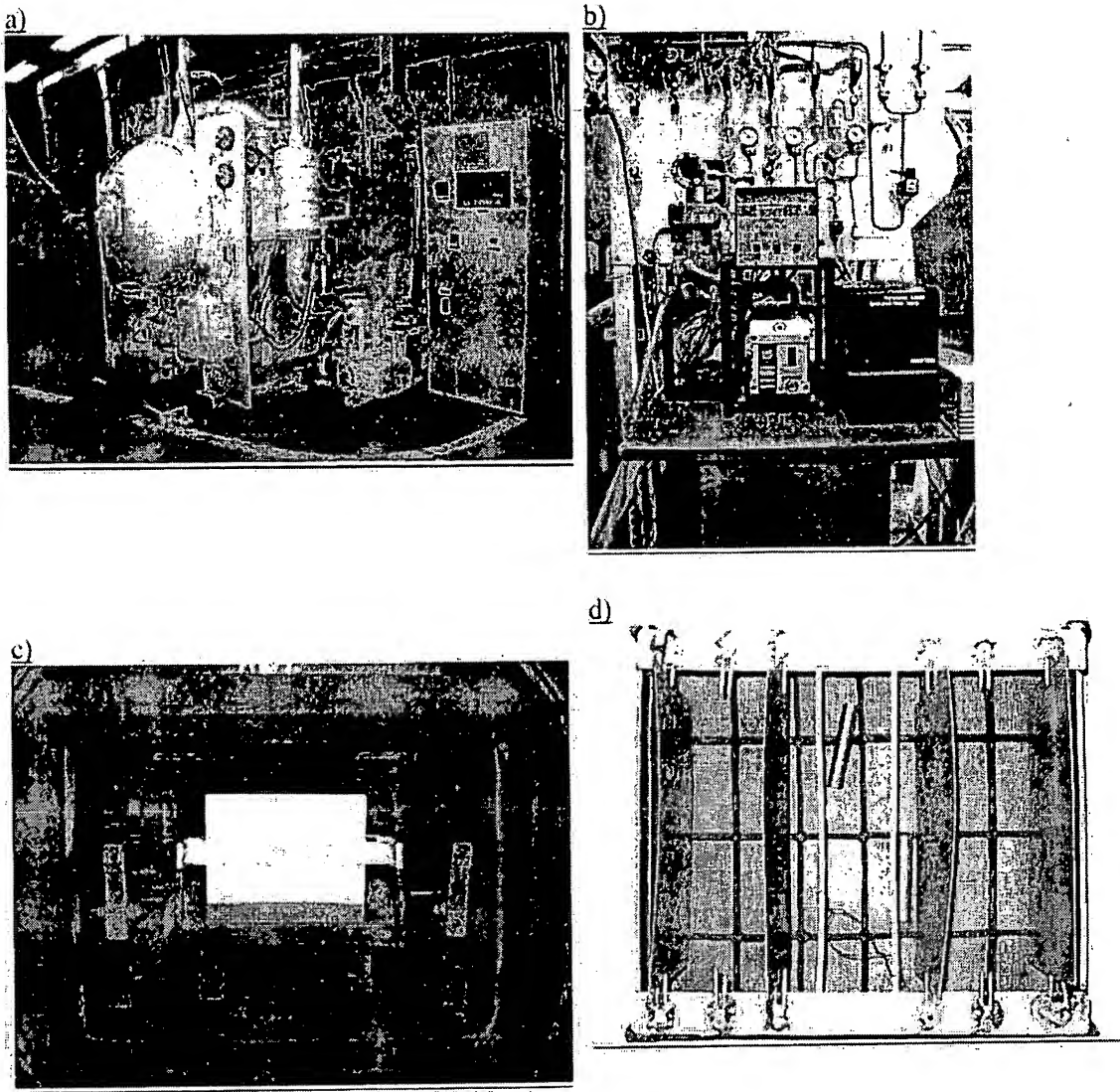
Figure. 1   Experimental equipment and charge arrangement: (a) vacuum carburizing furnace, (b) gas dosing system and mass spectrometer, (c) the charge in the furnace chamber and (d) the charge after process

Four different methods of gas dosing during the boost stage were tested in experimental tests and labeled as Experiment 1, Experiment 2, Experiment 3 and Experiment 4. Each of the Experiments were conducted at the same (1) pressure (5 mbar), (2) diffusion time (10 minutes), (3) boost time (20 minutes), and (4) temperature (950 $^{\circ}$C).

However, Experiment 1 was conducted using a carbon carrier with an acetylene/ethylene ratio 0.55 (i.e., the lower end of the acetylene to ethylene ratio recited in claim 1) blended with hydrogen at a ratio of 1:1 hydrogen to carbon carrier. Experiment 2 was conducted using a carbon carrier with an acetylene to ethylene ratio 0.428 (i.e., the ratio described in JP 765) blended with hydrogen at a ratio of hydrogen to carbon carrier of 1:1. Experiment 3 was conducted using a carbon carrier with an acetylene/ethylene ratio 0.428 and no hydrogen gas. Experiment 4 was also conducted using a carbon carrier with an acetylene/ethylene ratio 0.428 and no hydrogen gas, but at an increased carbon carrier flow rate (hydrocarbon consumption).

The parameters for Experiments 1-4 are illustrated below in Table 1.

Table 1

Parameter	Experimental 1	Experiment 2	Experiment 3	Experiment 4
Acetylene (A) flow rate (L/hr.)	33.6	28.5	30.8	57.0
Ethylene (E) flow rate (L/hr.)	61.4	66.5	71.8	133.0
Hydrogen (H) flow rate (L/hr.)	95.0	95.0	0	0
Ratio A/E	0.55	0.428	0.428	0.43
Ratio (A+E)/H	1	1	∞	∞
Temperature (°C)	950	950	950	950
Time of boost (min)	20	20	20	20
Time of diffusion (min)	10	10	10	10
Pressure (mbar)	5	5	5	5
Charge (m²)	0.4	0.4	0.4	0.4

During the boost stage, a mass spectrometer measured the chemical composition of the exhaust gases, including the hydrogen content. The amount of hydrogen in the exhaust

gases is a qualitative factor to determine the efficiency of a carbon transfer from a hydrocarbon gas mixture to a solid state. In other words, the greater the amount of hydrogen gas in the exhaust gas, the more efficient the carbon carrier has decomposed and adsorbed into the steel charge. Figure 2 illustrates the amount of hydrogen in exhaust gases for Experiment 1 and Experiment 2, whereas Figure 3 illustrates the absolute values of the amount of hydrogen content in exhaust gases for Experiments 1-3.

Furthermore, the creation of by products in the form of soot and/or tar was observed and detected on the surface of samples using SEM and EDS techniques after cooling the samples to ambient temperature. See Figures 4a-4d.
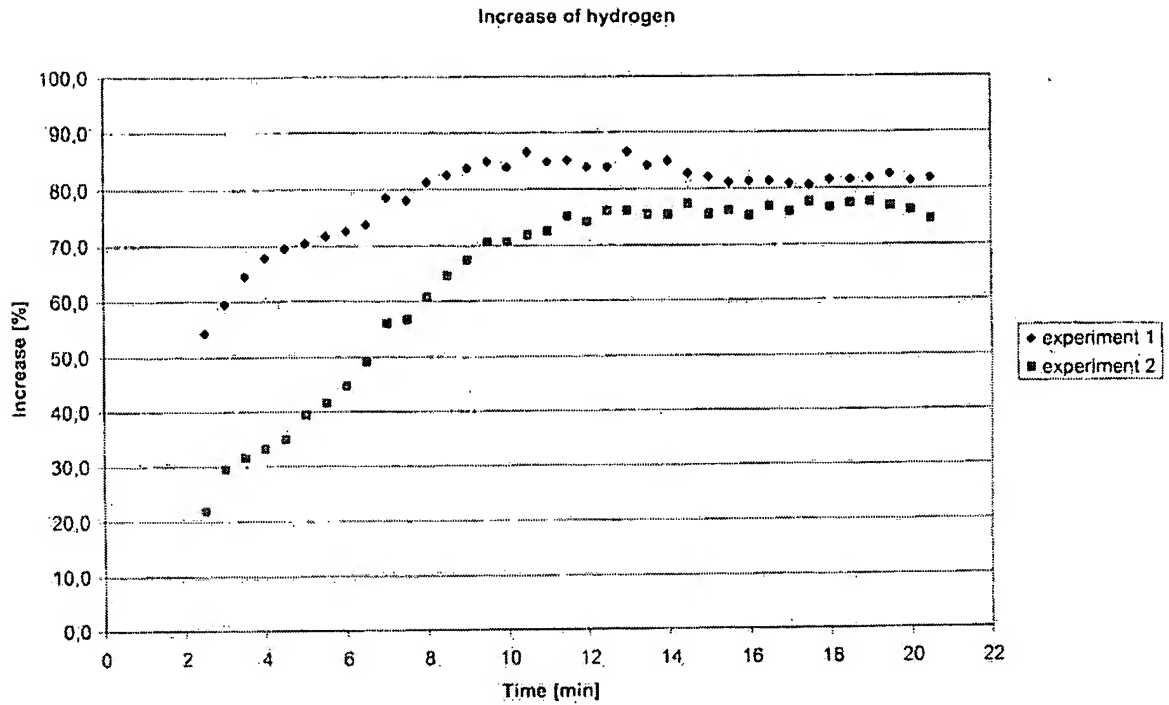
Increase of hydrogen

Fig. 2   The relative increment of hydrogen content during the boost stage for Experiment 1 and Experiment 2.
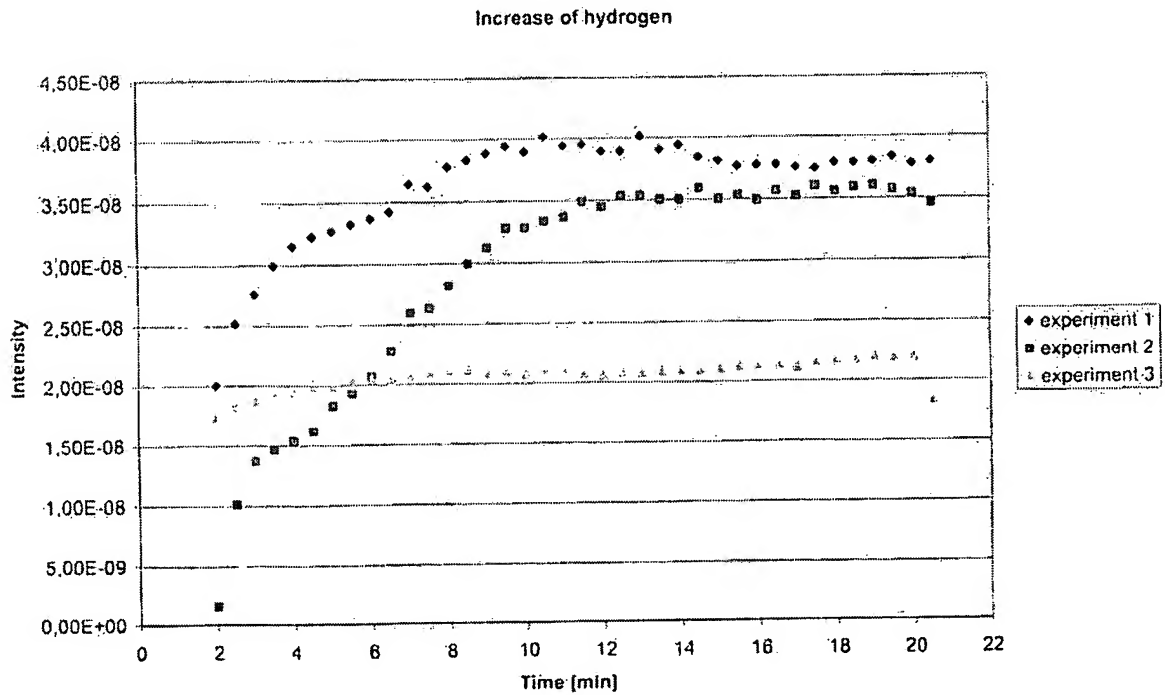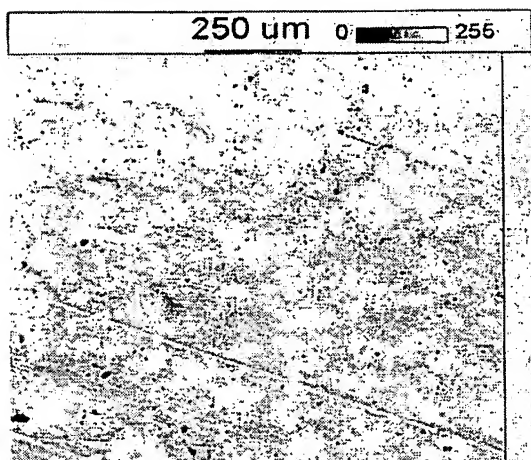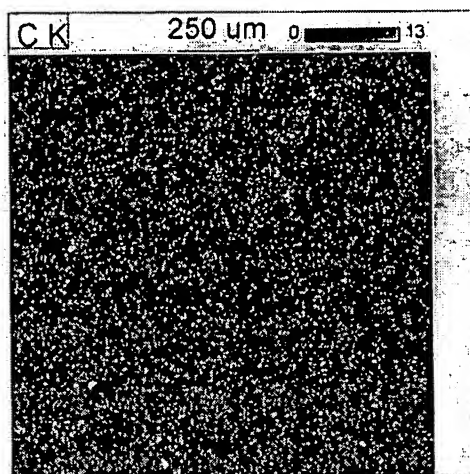
Increase of hydrogen

Fig. 3   The absolute increment of hydrogen content during the boost stage for Experiment 1 and Experiment 2.

a) Experiment 1 – SEM

EDS carbon analyze
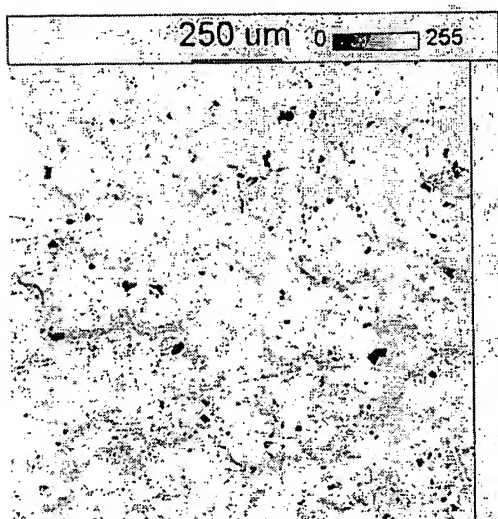

b) Experiment 2 – SEM

EDS carbon analyze
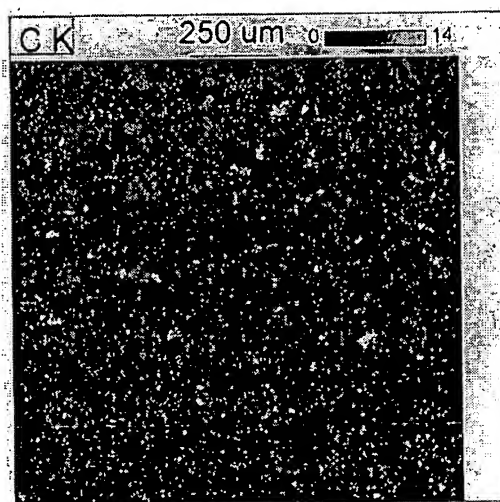
c) Experiment 3 – SEM

EDS carbon analyze

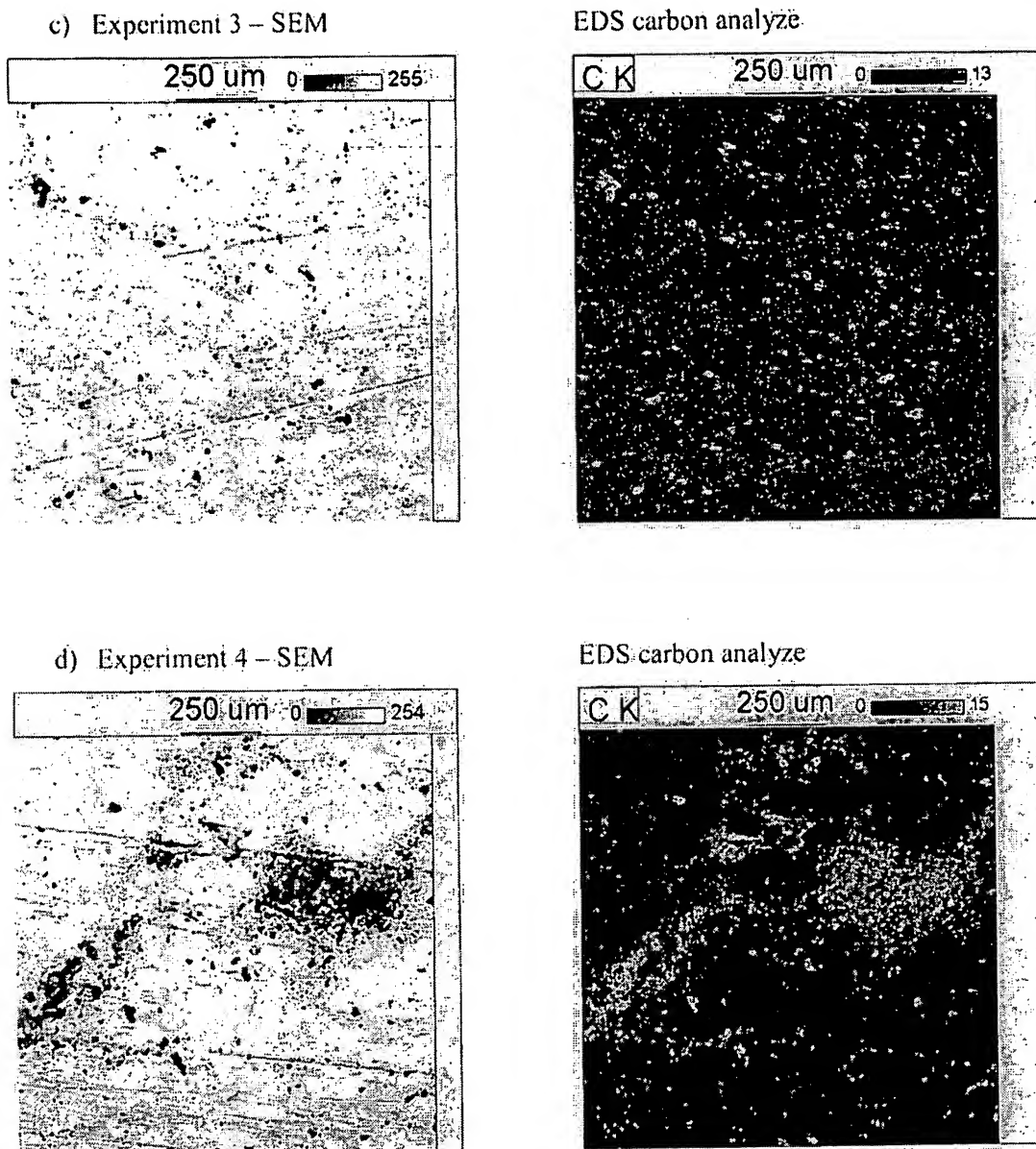d) Experiment 4 – SEM

EDS carbon analyze

Fig. 4   Comparison of the Presence of By-products (i.e., soot and tar) on the Surfaces of the Charge Samples after the Experiments 1-4.

As shown above in Figure 2, at a boost time of 20 minutes, the amount of hydrogen in Experiment 1 (0.55 acetylene to ethylene ratio) was approximately 81%, while the amount of hydrogen in Experiment 2 (i.e., 0.428 acetylene to ethylene ratio) was approximately 75%. Moreover, as shown above in Figure 4a, the charge of Experiment 1 displayed a perfect purity with only single microscopic scaled traces of soot and tar by-products remaining on the

samples in comparison to the charge of Experiments 2-4 (represented in Figure 4b-4d, respectively).

As such, the experimental results demonstrate that the presently claimed hydrocarbon gas mixture for the under-pressure carburizing of steel achieves unexpectedly improved hydrocarbon (i.e., acetylene and ethylene) decomposition together with a more efficient carbon transfer from a gaseous phase to steel even at lower end of the acetylene to ethylene ratio recited in claim 1 (0.55) in comparison to an acetylene to ethylene ratio 0.428 (i.e., the ratio disclosed in JP 765).

The experimental results also demonstrate that the inclusion of hydrogen as the third component of a hydrocarbon gas mixture unexpectedly improves hydrocarbon decomposition. As shown in Figure 3, the three-component mixture used in Experiment 1 and Experiment 2 (i.e., acetylene to ethylene ratio of 0.55 and 0.428, respectively) had a significantly greater absolute hydrogen content than Experiment 3 (i.e., acetylene to ethylene ratio 0.428 and no hydrogen gas). Furthermore, hydrocarbon decomposition for Experiment 2 is importantly less than Experiment 1, especially in the initial period of boost stage (i.e., 12 min). This is especially beneficial for multiphase boost/diffusion vacuum carburizing processes.

Thus, the above results demonstrate that the acetylene to ethylene ratio of 0.55 to 2 is necessary to achieve a uniformly carburized layer with no accumulation of soot or tar. JP 765, with an acetylene/ethylene ratio outside of this range, does not achieve such results.

6.   I hereby declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine and/or imprisonment under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing therefrom.

Date: May 09, 2008
Piotr Kula